Role of Gas Diffusion in Bloater Formation of Brined Cucumbers

K. A. COREY, D. M. PHARR, and H. P. FLEMING

ABSTRACT –

A method was developed to measure diffusion rates of CO_2 and N_2 through fresh and brined cucumber tissue to examine the role of gas diffusion in bloater formation. The diffusion rate of CO_2 was 3.2 times greater than N_2 through fresh and 2.4 times greater than N_2 through brined cucumber tissue. The ratio of the diffusion rates of CO_2 to N_2 through brined cucumbers was not significantly altered from that of fresh fruit. Solubility of gases was determined to be a factor governing the rate and extent of bloater damage. Maximum rates of increase in expansion volume of N_2 -exchanged cucumbers was 0.42, 1.30, and 11.90% hr⁻¹ for brines purged with Ar, CO_2 , and SO_2 , respectively, and 0.89% hr⁻¹ for Ar-exchanged fruit following purge of the brine with CO_2 .

INTRODUCTION

THE PRODUCTION of carbon dioxide by fermentative microorganisms has long been implicated as the cause of bloater damage in pickling cucumbers (Veldhuis and Etchells, 1939; Etchells et al., 1945). However, only recently has a detailed mechanism for bloater formation of pickling cucumbers been proposed (Fleming and Pharr, 1980). It was hypothesized that a liquid clogged layer of tissue develops in brine-stored cucumbers due to the entrance of brine. This liquid-clogged region of tissue was further postulated to serve as a differentially permeable barrier to the diffusion of N₂ and CO₂. Since a large portion of the internal gas atmosphere of a cucumber prior to brining is N₂, and the CO₂ concentration in the brine increases rapidly upon fermentation (Fleming et al., 1973b), a diffusion gradient for CO₂ arises toward the fruit interior. It was further hypothesized that considering the much greater aqueous solubility of CO₂ than N₂ (Hodgman et al., 1958), there is a greater inward transport of CO₂ than outward transport of N2, resulting in an internal gas pressure in excess of atmospheric pressure. This may then cause the tissue to rupture with resultant formation of a gas pocket (bloater).

Diffusion of gases through apples and other fruits has been found to be governed by Fick's first law of diffusion (Burg and Burg, 1965). This relationship describes the amount of some diffusing species i, crossing a certain area per unit time, e.g. moles of a solute per cm² in a second. For one dimension, the law may be written as:

$$J_{i} = -D_{i}\partial C_{i}/\partial x \tag{1}$$

where J_i = flux (moles/cm²-s), D_i = diffusion coefficient (cm²/s), and $\partial C_i/\partial x$ = concentration gradient in the x - direction (moles/cm⁴). Frequently in the study of gas transfer through biological tissue, gas diffusion through different phases must be considered. For this reason a diffusion

Author Pharr is affiliated with the Dept. of Horticultural Science, North Carolina State Univ., Raleigh, NC 27650. Author Corey, formerly with North Carolina State Univ. is currently with the Dept. of Horticulture, Univ. of Maryland, College Park, MD. Author Fleming is with the USDA-ARS, Food Fermentation Laboratory and Dept. of Food Science, North Carolina State Univ., Raleigh, NC 27650.

coefficient expressed in terms of a pressure gradient is more convenient than the use of concentration gradient as described in Eq (1). In addition, the solubility of a gas is a major factor governing its transport rate through a liquid (Krogh, 1919; Guyton, 1971). Fenn and Rahn (1964) incorporated this solubility factor, replaced concentration with partial pressure, and isolated area from flux to yield the following form of Fick's first law:

$$dQ_i/dt = -A\alpha_i D_i \partial P_i/\partial x \qquad (2)$$

The expression dQ_i/dt is the instantaneous rate of movement of a gas perpendicularly across an area A driven by a partial pressure gradient $\partial P_i/\partial x$, where P_i is the partial pressure of the gas species and x is the distance. The diffusion coefficient D, frequently expressed in cm²/s, is a property of both the medium and the diffusing substance. The two constants α D represent an analog to Krogh's diffusion coefficient where α is the Bunsen solubility coefficient. When applied to gas diffusion through fruits, the surface area term in the equation is in actuality the effective surface area. For apples, this represents the surface area of lenticels (Burg and Burg, 1965) and for cucumbers may be the total surface of the stomatal pores. Total stomatal pore area has been estimated by Smith et al. (1979) to be about 0.062% of the total surface area for large 'GY14' cucumbers.

According to the hypotheses of Fleming and Pharr (1980) the diffusion rates of CO₂ and N₂ for a given partial pressure gradient through fresh cucumbers should be nearly the same for both gases due to the relatively continuous nature of the intercellular spaces. However, if a liquid-clogged layer of tissue develops in fruit upon brine storage as hypothesized, the diffusion rate of CO₂ should be greater than for N₂ due to the presence of a liquid barrier to diffusion. In addition, the rate of increase in expansion volume of brine to the exterior of cucumbers, could be expected to be dependent on the difference in solubilities of gases inside the fruit and in the brine.

This study was conducted to examine the role of gas diffusion on bloater damage in pickling cucumbers. Specific objectives were to: (1) develop a method to measure and compare diffusion rates of CO₂ and N₂ through fresh and brined cucumbers and (2) test the hypothesis that gas solubility is a major factor governing the rate and extent of bloater damage in pickling cucumbers due to the effect of solubility on the diffusion rate of a gas in a liquid system.

MATERIALS & METHODS

Cucumbers

Size no. 3 pickling cucumbers (3.8-5.1 cm diam), cv. Calypso, were obtained from a local grower and from field plots at University Research Unit 4 at Raleigh. Following harvest, cucumbers were washed, humidified with moist cloths and held in $13.0 \pm 1.0^{\circ}$ C storage for not longer than 7 days. Fruit were equilibrated at $22.0 \pm 1.0^{\circ}$ C prior to experimental use.

Gas diffusion apparatus

Ends of cucumbers were removed perpendicular to the longitudinal axis of the fruit, and a 5.0 cm length, approximately cylindrical shaped section was taken. A 2.0 cm diam cavity was made

through the center of each fruit with a cork borer, which removed most of the seed region. All cut surfaces were blotted to remove liquid expressed from cut cells. Individual cucumber segments were then placed in the diffusion apparatus (Fig. 1). Gas tight seals were made at the junctions of: (1) each end of the segment and the two rubber gaskets, (2) the bottom rubber gasket and the apparatus platform, and (3) the beaker and bottom rubber gasket. The seals were made with a stiff, nonmelting, silicone, high vacuum grease (Cat. No. 970 V; Dow Corning Corp., Midland, MI).

Gas diffusion measurements

An experiment was conducted to test if dQi/dt was linearly related to ΔP_i for diffusion of CO₂ and N₂ through fresh cucumber segments using the diffusion apparatus (Fig. 1). This was achieved by determining the steady state diffusion rates of both CO2 and N2 for different partial pressure gradients of the respective gases. Various humidified (bubbled gases through water) mixtures of CO2 and N2 were flowed into the internal gas cavity of the cucumber segments through the gas cavity inlet at a rate of 250 ml/min. Measurement of CO₂ diffusion from the internal gas cavity through the surface of the cucumber segment was achieved by flowing pure N2 through the chamber at 25 ml/min and analyzing the gas composition of a 0.5 cm³ sample of gas taken from the chamber sampling port with a gas chromatograph.

Diffusion of N₂ was measured by using CO₂ as the chamber gas. Attainment of a steady state diffusion rate was presumed when there was no change in composition of the chamber outlet gas over time. Measurements of CO₂ and N₂ diffusion rates were made on

separate cucumber segments.

An additional experiment was designed to compare the diffusion rates of CO₂ and N₂ through fresh and brine-stored (72 hr) cucumbers. Diffusion rates for both CO₂ and N₂ were measured on the same cucumber segments for a partial pressure difference (ΔP_i) of about 1 atmosphere (i.e. pure CO_2 in the gas cavity and pure N2 in the chamber; and the converse). The ratio of the diffusion rates of CO₂ to N₂ was calculated for each segment.

Gas exchange of cucumbers and brine

The effect of differences in the aqueous solubility of gases inside the fruit and in the exterior brine on bloater damage was tested using three paired combinations of CO₂, N₂, and Ar. These gases differ appreciably with respect to their solubilities in water and aqueous NaCl solutions (Table 1). Data for the same concentration of NaCl solution were not found in the literature. However, the solubility of each gas is decreased markedly in aqueous NaCl solutions of concentrations comparable to that used in this study. In water (25°C), CO₂ is 53.1 times more soluble than N₂ and 24.2 times more soluble than Ar; and Ar is 2.2 times more soluble than

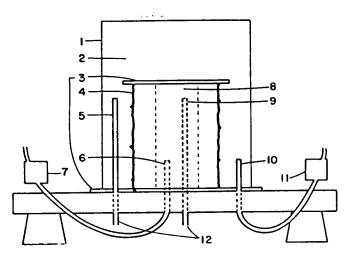


Fig. 1-Schematic diagram of the diffusion apparatus: (1) glass beaker; (2) chamber; (3) rubber gasket; (4) cucumber segment; (5) chamber inlet; (6) gas cavity outlet; (7) gas cavity sampling port; (8) internal gas cavity; (9) gas cavity inlet; (10) chamber outlet; (11) chamber sampling port; (12) flow meter leads.

N2. These three comparisons of aqueous solubilities formed the basis of three experimental treatments.

Cucumbers (1.7 kg) were packed into 3.8 liter jars to give a 45:55 (w/v) pack-out ratio of fruit to brine. Each jar lid was equipped with a glass gas dispersion tube, graduated reservoir and glass rod to support the reservoir as described previously by Fleming and Pharr (1980). For each gas pair treatment, the internal atmospheres of fruit were exchanged with the less soluble gas of a gas pair at a flow rate of 300 ml/min. Acidified, aqueous NaCl solution was added to the jars, while maintaining gas flow to exclude air from the system. The brining medium was 10.6% (w/w) NaCl, 0.32% (v/v) glacial acetic acid, and 0.20% (w/v) sodium benzoate. The acidified, aqueous NaCl solution containing sodium benzoate was used to suppress microbial growth during storage (Fleming et al., 1980). Following addition of brine, a flow of the less soluble gas was continued at a rate of 50 ml/min for 48 hr. This length of time in brine storage was shown previously to bring about a bloater susceptible condition in artificially carbonated cucumbers (Fleming et al., 1978). After 48 hr brine storage, flow of the more soluble gas of a gas pair was initiated at a high flow rate (300 ml/ min) for 20 min in order to bring about a rapid saturation of the exterior brine. The flow rate was adjusted to 50 ml/min thereafter. A continuous N2-purge served as the control. "Expansion volume" of the brined cucumbers was determined by the rise in brine level in the graduated reservoir and was expressed as a percentage of the volume of cucumbers (Fleming et al., 1973a). Cucumbers were evaluated for bloater damage according to Etchells et al. (1974) and bloater indices calculated according to Fleming et al. (1977).

An additional treatment with SO₂ as the gas in the exterior brine and N₂ as the exchange gas was used to determine the effect of an extreme solubility difference on the rate of expansion. The Bunsen solubility coefficient of SO₂ in water at 25°C is 30.0287 cm³ gas/cm³ H₂O (Hodgman et al., 1958), which is 2100 times greater than the value for nitrogen. Due to the extremely high aqueous solubility of SO2, a flow of 300 ml/min would have been too low to bring about a rapid near saturation of the brine. Therefore, the flow of SO₂ through the brine was made sufficiently rapid to produce free gas bubbles at a rate that was visually estimated as comparable to the other gas treatments.

Regression analysis

Second-order polynomials, forced through the origin, were fit to the percentage expansion volume data. A comparison of the rates of increase in expansion volume for the gas pair treatments was of interest, since this response was presumably governed by the rates at which the various gases diffused into and out of the cucumbers. Therefore, the coefficients of the first-order terms in the second-order regression equations were compared. This coefficient represents the maximum rate of expansion and is equivalent to the slope of the tangent to the regression curve through the origin.

RESULTS

Gas diffusion

The relationship of diffusion rate (dQi/dt) to partial pressure difference (ΔP_i) for both CO_2 and N_2 through fresh cucumber segments was approximately linear (Fig.

Table 1-Solubility of gases in water and aqueous NaCl solutions at 25°C

	α ^a (cm ³ gas/cm ³ solution)		
Gas	H ₂ O	Aqueous NaCl solution ^d	
COo	0.7590 ^b	0.4585 (10.9) ^e	
No.	0.0143 ^b	0.0052 (11.9) ^f	
CO ₂ N ₂ Ar	0.0314 ^c	0.0216 (15.9) ^g	

 $^{^{2}}$ α denotes the Bunsen solubility coefficient; the volume of gas when reduced to 0°C and 1 almosphere, absorbed by one volume of solution when the pressure of the gas itself is 1 atmosphere. b From Hodgman et al. (1958)

From Lannung (1930)

9 From Akeriof (1935)

d Parenthetical values are the % NaCl (w/w) as calculated from other concentration units given in the references cited in this table. From Fleming et al. (1975) From International Critical Tables (1928)

2). This was expected and verified that Fick's first law of diffusion applied to gas diffusion through cucumbers as measured with the apparatus diagrammed in Fig. 1.

The diffusion rate of CO₂ was significantly greater than N₂ through both fresh and brine-stored cucumber segments (Table 2). Also, the diffusion rate of CO₂ was significantly decreased upon brine storage. A trend toward a reduction in the diffusion rate of N2 in brine-stored compared to fresh cucumbers was measured. The ratio of CO₂ to N₂ diffusion rates did not change significantly upon brine storage.

Expansion volume and bloater damage

The largest increase in expansion volume was obtained for N₂ (in)-CO₂ (out) (Fig. 3); the gas pair having the greatest difference in aqueous solubility (Table 1). Gas pairs with less difference in solubility resulted in correspondingly less increase in expansion volume. This trend was the same for both experiments (Fig. 3). The maximum rates of increase in expansion volume (average of estimates of linear term coefficients) for the different gas pairs were all significantly different and increased with increasing difference in the solubilities' of the gases in a pair (Table 3). The same trend existed for the bloater index values. However, a statistically significant difference was detected only between N2(in)-CO2(out) and the control.

When SO₂ was charged rapidly through the brine surrounding cucumbers stored for 48 hrs in brine under a continuous N2-purge, expansion volume increased to over 5% within 1 hr (Fig. 4). The maximum rate obtained from

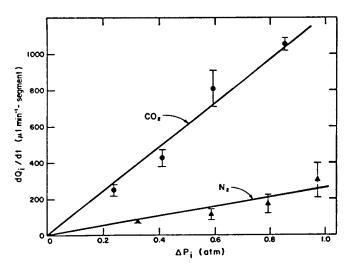


Fig. 2-Steady state diffusion rates (dQ/dt) of CO2 and N2 through fresh cucumber segments as influenced by the partial pressure difference ΔP_i , where $\Delta P_i =$ the partial pressure of the ith gas in the internal gas cavity less the partial pressure of the same gas in the chamber. Each point represents the mean of three replications. Vertical bars represent ± one standard error of the mean.

the second-order polynomial was 11.9% hr⁻¹, which was over nine times the maximum rate estimated for the N2-CO₂ gas pair.

DISCUSSION

FLEMING AND PHARR (1980) proposed that there is a differential flux of CO₂ and N₂ through brined cucumbers, leading to the development of internal gas pressure upon carbonation of the brine, with subsequent bloater damage. The observation that bloater damage is minimal in cucumbers carbonated immediately following brine addition (Fleming et al., 1978; Corey et al., 1983) was proposed to be due to the following: "... N₂ is displaced from the cucumbers by CO₂ before intercellular gas spaces become clogged and restrict the rate of N2 removal from the

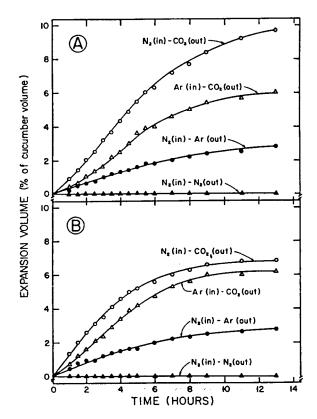


Fig. 3-Expansion volume changes of brined cucumbers as influenced by various gas pairs, used to exchange the internal atmospheres of fresh pickling cucumbers and to saturate the exterior brine following 48 hr brine storage. The first gas given for a gas pair (in) denotes the gas used to exchange the internal atmosphere of fruit before brining, and the second (out) denotes the gas used to saturate the brine after the fruit was gas-exchanged and then brined. The A and B denote the same experiment conducted with two different cucumber harvests at two separate times. See Table 3 for related

Table 2-Diffusion rates (dQ/dt) of CO2 and N2 through fresh and brine-stored cucumber segments

Cucumbers	dQ/dt (μ/ min ⁻¹ – segment) ^a		Row	
	CO ₂	N ₂	comparison	CO2/N2ª
Fresh	655.4 ± 15.5	219.1 ± 43.6	• #	3.20 ± 0.52
Brine-stored (72 hr) Column comparison	360.2 ± 63.6	158.5 ± 20.1 NS ^b	•	2.40 ± 0.67 NS

Mean of three replications ± standard error of mean

NS = Not significant

* = significant at P = 0.05

^{** =} significant at P = 0.01

tissue." Their hypothesis was supported by the demonstration of a reduced rate of CO2 removal from brined compared to fresh cucumbers that were CO2-exchanged prior to brine storage, with a simultaneous reduced rate of N₂ entrance in brined cucumbers upon N₂-purging. Hence, fresh cucumbers were proposed to exchange more rapidly with the ambient gaseous environment than brine-stored fruit due to the formation of a "continuous liquid-clogged outer layer" of tissue in brined fruit. Considering the much greater solubility of CO₂ than N₂, this implied that the ratio of the diffusion rates of CO₂ to N₂ for brined cucumbers would be considerably higher than for fresh cucumbers. Results of the present study are not in agreement with this idea (Table 2). Differential diffusion rates of CO2 and N2 were measured through both fresh and brine-stored cucumbers. However, a significant change in the ratio of dQCO2/dt to DQN2/dt upon brining was not detected.

A reduction in the internal gas volume of cucumbers held in brine storage has been measured previously (Corey et al., 1983). This suggests that the number of barriers to gas exchange increases in brine-stored cucumbers and hence the resistance to gas diffusion should increase accordingly.

Table 3—Effects of different gas pair combinations used to exchange the internal atmospheres of cucumbers and to saturate the brine on maximum rate of increase in expansion of exterior brine volume and bloater damage^a

Gas pair (in-out) ^b	Δ solubility of gases (cm ³ gas/cm ³ H ₂ O) ^c	Max rate of increase in expansion vol (% hr ⁻¹) ^d	Bloater index ^d
N ₂ - N ₂ (control)	0	0	0
$N_2 - Ar$	0.017	0.42	9.3
Ar - CO ₂	0.728	0.89	11.1
$N_2 - CO_2$	0.745	1.30	26.4
LSD (0.05)		0.23	18.4

Values are means of duplicate 3.8 liter jars each containing 12—14 cucumbers
 Laterals and a second of cucumbers and a second of cucumbers.

d Coefficient of correlation between max rate of increase in expansion volume and bloater index was 0.87 (P = 0.01).

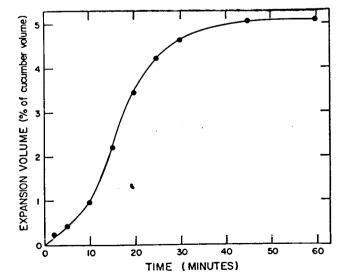


Fig. 4—Expansion volume changes of brined cucumbers charged with SO₂ following 48 hr brining under a continuous N₂-purge. Cucumbers were N₂-exchanged before brine storage.

Although a reduction in the diffusion rates of both CO_2 and N_2 was measured in brined compared to fresh fruit (Table 2), most important was the fact that the ratio of dQ_{CO_2}/dt to dQ_{N_2}/dt was not altered substantially upon brine storage of cucumbers. If a 'continuous' liquid-clogged barrier to gas diffusion develops in brine-stored cucumbers, then the ratio of dQ_{CO_2}/dt to dQ_{N_2}/dt should be substantially higher than for the same ratio in fresh cucumbers.

Interpretation of diffusion rates

A possible explanation for the lack of difference in the ratio of dQ_{CO_2}/dt to dQ_{N_2}/dt in brined compared to fresh cucumbers may be due to the absence of a continuous liquid-clogged region of tissue in brined cucumbers. A simplified model will aid in the interpretation of the diffusion rates of CO_2 and N_2 measured experimentally.

The intercellular gas channels may be conceived to be analogous to small capillary tubes. In both fresh and brined cucumbers, some of these passages may be blocked with continuous liquid barriers (Fig. 5A). Other gas channels may be relatively unblocked, containing a liquid film along the sides of the channel, but possessing a continuous gas phase channel throughout the length of the tube (Fig. 5B). For a continuous gas phase channel, the diffusion rates of CO₂ and N₂ would be expected to be equal. The binary diffusion coefficient for the CO₂-N₂ gas pair in the gas phase, denoted by DCO₂-N₂, is 0.16 cm²/s-atm (Fenn and Rahn, 1964). Since DCO₂-N₂ = DN₂-CO₂, the same value may be used to describe the gas phase diffusion of both CO₂ and N₂. Therefore, dQCO₂/dt from a to c should be equal to dQN₂/dt from c to a in Fig. 5B.

Suppose, that a relatively thin continuous liquid barrier (e.g. 5 cell layers thick) develops in cucumbers upon brining. Assuming an average cell diameter of approximately 24μ , the thickness of this barrier would be 1.2×10^{-2} cm. The average path length from the cavity-tissue interface to the surface of the cucumber was measured to be 8.0×10^{-1} cm. The simplified model of Fig. 5A may be applied to this situation. Let the distances ac = 8.0×10^{-1} cm and $\overline{ab} = 1.2 \times 10^{-2}$ cm, the thicknesses of the liquid barrier and the remaining gas phase distance respectively. Further, assume that the liquid barrier behaves essentially as an aqueous barrier. The absolute diffusion coefficient of CO₂ in H₂O at 22°C is 1.91×10^{-5} cm²/s and for N₂ is 2.02×10^{-5} cm²/s (International Critical Tables, 1929). However, if these values are multiplied by their respective Bunsen

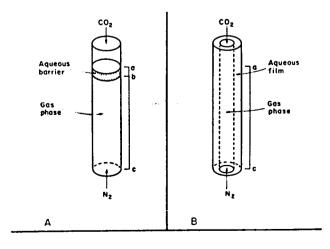


Fig. 5—Schematic representation of: (A) capillary tube with a continuous aqueous barrier to diffusion of CO₂ and N₂ and (B) capillary tube lined with an aqueous film containing a continuous gas channel for diffusion of CO₂ and N₂. See text for discussion.

b Internal atmospheres of cucumbers were exchanged with the less soluble gas in a pair (first gas), followed by a purge of the same gas for 48 hr following addition of brine. Flow of the more soluble gas in a pair (second gas) was begun after 48 hr brine storage.

C See also Table 1.

solubility coefficients at 22°C (Hodgman et al., 1958), the diffusion coefficient $D' = \alpha_i D_i$ is defined, where D_i is the absolute diffusion coefficient in water. Hence, D'CO2 = 1.45 \times 10⁻⁵ cm²/s-atm and D'N₂ = 3.0 \times 10⁻⁷ cm²/satm. Experimentally, dQi/dt was determined in the steady state. Applied to the capillary tube model this means that dQi/dt is the same for any point along the path ac. In addition, for pure CO2 at one end of the tube and pure N2 at the other in a flowing system, the partial pressures of the gases at points a and c are given as follows:

$$Pa(CO_2) = 1$$
, $Pc(CO_2) = 0$ and $Pa(N_2) = 0$, $Pc(N_2) = 1$

Letting $X_1 = \overline{ab}$ and $X_2 = \overline{bc}$, substituting D_i' for $\alpha_i D_i$, assuming steady state conditions, and applying Eq (2) yields the following relationship to describe diffusion of CO₂ from point a to point c in the capillary of Fig. 5A.

$$dQ_{CO_2}/dt = \frac{AD'_{CO_2}}{X_1}(P_a - P_b) = \frac{AD_{CO_2 - N_2}}{X_2}(P_b - P_c) \quad (3)$$

Similarly, for diffusion of N₂ from point c to point a;

$$dQ_{N_2}/dt = \frac{AD_{N_2-CO_2}}{X_2}(P_c-P_b) = \frac{AD'_{N_2}}{X_1}(P_b-P_a)$$
 (4)

Substituting the appropriate values and solving for Pb for each gas yields, $P_b(CO_2) = 5.9 \times 10^{-3}$ atm and $P_b(N_2)$ = 9.9 x 10^{-1} atm. Substituting the respective values for P_b into Eq (3) and (4) gives $dQ_{CO_2}/dt = (1.2 \times 10^{-3} \text{ cm/s})$ (A) and $dQ_{N_2}/dt = (2.5 \times 10^{-5} \text{ cm/s})$ (A). Taking the ratio of dQcO₂/dt to dQN₂/dt gives a value of 48, which is nearly equal to $\alpha_{CO_2}/\alpha_{N_2}$. Thus, a barrier of a continuous nature must not develop in cucumbers stored in brine for short periods of time (e.g. 72 hr) since the ratio of dQ_{CO2} dt to dQ_{N_2}/dt was only 3.2 (Table 2). This finding is in contrast to the 'continuous' liquid clogged region of tissue proposed previously to occur in brined cucumbers (Fleming and Pharr, 1980). Reduction in the absolute values of dQCO2/dt and dQN2/dt upon brining implies that the number of capillaries analogous to Fig. 5A must increase in brine-stored fruit. However, because the ratio of diffusion rates of CO₂ to N₂ more nearly approaches the expected value for pure gas phase diffusion, there must be some proportion of intercellular avenues analogous to the capillary of Fig. 5B. In actuality, the continuous gas channels present in brined cucumbers are probably extremely tortuous. The proportion of the total gas avenues analogous to the capillary of Fig. 5B, denoted by p, may be approximated using the experimentally determined value for the ratio of dQ_{CO2}/dt to dQ_{N2}/dt through brined fruit by the following equation.

$$\frac{dQ_{CO_2}/dt}{dQ_{N_2}/dt} = \frac{pD_{CO_2}-N_2 + (1-p)D'_{CO_2}}{pD_{N_2-CO_2} + (1-p)D'_{N_2}}$$
(5)

Substituting values and solving for p gives $p = 6.15 \times 10^{-5}$. This calculation demonstrates that the presence of an extremely small number of continuous gas channels may result in an overriding effection the diffusion rates of 2 gases (e.g. CO_2 and N_2) differing greatly in solubility.

Internal gas pressure development in freshly brined cucumbers upon carbonation of the brine is an expectation based on the difference in CO2 and N2 diffusion rates measured through cucumber tissue in this work and has been experimentally measured (Corey et al., 1983). Since the ratio of dQ_{CO2}/dt to dQ_{N2}/dt was not found to be different for fresh and brined cucumbers, the lower internal gas pressure measured in freshly brined compared to brinestored cucumbers (Corey et al., 1983) may be attributed to mass exit of gases through fresh cucumbers upon internal pressurization. This is consistent with the evidence of Corey et al., (1983) for the occurrence of mass flow through fresh cucumbers in brine. Resistance to mass flow of gases in fresh cucumbers is much less than in brined cucumbers. Therefore, both diffusion and mass flow of gases are important processes regulating the internal gas pressure of freshly brined cucumbers upon carbonation of the brine, whereas transport of gases in brine-stored cucumbers is probably limited to diffusion.

Influence of gas solubility on bloater damage

The rate of increase in expansion volume and bloater damage in brined cucumbers was shown to be strongly dependent on the difference in aqueous solubility of gases inside the fruit and in the exterior brine (Fig. 3, 4 and Table 3). The differences in the maximum expansion rates for the gas pairs was presumably due to differential rates of diffusion of the two gases in a given gas pair treatment. Since solubility is a factor governing the diffusion rates of gases through both the fruit tissue and the brine; a greater amount of the more soluble gas diffuses into the fruit than the less soluble gas out of the fruit in a given time as proposed by Fleming and Pharr (1980). This results in an internal gas pressure in excess of atmospheric pressure and was measured by Corey et al. (1983) for the gas pair N₂-CO₂. The extent of boater damage for the different gas pairs (Table 3) may vary due to variations in the rate and extent of internal gas pressure development. In addition, the relationships of maximum rate of increase in expansion volume and bloater index to Δ solubility as determined are not clearly defined, though a definite trend is evident (Table 3). The role of gas solubility as it governs diffusion of gases through the brine as compared to through the cucumber tissue has not been evaluated. Preservative concentration (e.g. sodium benzoate) and pH also influence gas solubility. Their effects on transfer rates of different gases also needs evaluation. Although solubility of gases has a strong influence on their relative diffusion rates, other factors may influence gas transport through fresh and brined cucumbers. Changes in the effective surface area for diffusion of gases, permeability of the cuticle, molecular sieve effects, and pH are a few such factors that may have an effect on the differential diffusion rates of gases through cucumbers. These may be important additional considerations in studying the mechanism of bloater formation in brined cucumbers.

REFERENCES

Åkerlof, Gösta. 1935. Solubility of noble gases in salt solutions at 25°C. J. Am. Chem. Soc. 57: 1196.

Burg, S.P. and Burg, E.A. 1965. Gas exchange in fruits. Physiol.

Plant. 18: 870.

Corey, K.A., Pharr, D.M., and Fleming, H.P. 1983. Role of the osmoticum in bloater formation of pickling cucumbers. J. Food Sci. 48: 197.

Etchells, J.L., Bell, T.A., Fleming, H.P., Kelling, R.E., and Thompson, R.L. 1974. Bloater chart. Published and distributed by Pickle Packers International, St. Charles, IL. Etchells, J.L., Fabian, F.W., and Jones, I.D. 1945. The Aerobacter

fermentation of cucumbers during salting. Mich. Agr. Exp. Sta.

Tech. Bull. No. 200.

Fenn, W.O. and Rahn, H. (Ed.) 1964. "Handbook of Physiology,"

Vol. 1, Sec. 3. Ch. 3: The physics of gases, Ch. 33: Diffusion of

gases.
 Fleming, H.P., Etchells, J.L., Thompson, R.L., and Bell, T.A. 1975.
 Purging of CO₂ from cucumber brines to reduce bloater damage.
 J. Food Sci. 49: 1304.
 Fleming, H.P. and Pharr, D.M. 1980. Mechanism for bloater formation in brined cucumbers.
 J. Food Sci. 45: 1595.
 Fleming, H.P., Thompson, R.L., Bell, T.A., and Monroe, R.J. 1977.
 Effect of brine depth on physical properties of brine-stock cucums.

Fleming, H.P., Thompson, R.L., Bell, T.A., and Monroe, R.J. 1977. Effect of brine depth on physical properties of brine-stock cucumbers. J. Food Sci. 42: 1464. Fleming, H.P., Thompson, R.L., Etchells, J.L., Kelling, R.E., and Bell, T.A. 1973a. Bloater formation in brined cucumbers fermented by Lactobacillus plantarum. J. Food Sci. 38: 499. Fleming, H.P., Thompson, R.L., Etchells, J.L., Kelling, R.E., and Bell, T.A. 1973b. Carbon dioxide production in the fermentation of brined cucumbers. J. Food Sci. 38: 504. —Continued on page 399

Volume 48 (1983)-JOURNAL OF FOOD SCIENCE-393

Fleming, H.P., Thompson, R.L., and Monroe, R.J. 1978. Susceptibility of pickling cucumbers to bloater damage by carbonation. J. Food Sci. 43: 892.

Guyton, A.C. 1971. "Textbook of Medical Physiology," 4th ed. W.B. Saunders Co., Philadeiphia.

Hodgman, C.D., Weast, R.C., and Selby, S.M. 1958. "Handbook of Chemistry and Physics," 40th ed., Chemical Rubber Publishing Co., Cleveland, OH. Thompson, R.L., and Monroe, R.J. 1978. Suscepti-

- "International Critical Tables." 1928. Vol. 3, p. 275. McGraw-Hill Book Co., New York.
 "Internatinal Critical Tables." 1929. Vol. 5, p. 63. McGraw-Hill

- Book Co., New York. Krogh, A. 1919. The rate of diffusion of gases through animal tissues, with some remarks on the coefficient of invasion. J. Physiol. sues, with 52: 391.
- Lannung, A. 1930. The solubilities of helium, neon, and argon in water and some organic solvents. J. Am. Chem. Soc. 52: 68. Smith, K.R., Fleming, H.P., Van Dyke, C.G., and Lower, R.L. 1979. Scanning electron microscopy of the surface of pickling cucumber fruit. J. Amer. Soc. Hort. Sci. 104: 528.

Veldhuis, M.K. and Etchells, J.L. 1939. Gaseous products of cucumber pickle fermentations. Food Res. 4: 621. Ms received 8/20/82; revised 11/5/82; accepted 11/11/82.

Paper No. 8465 of the journal series of the North Carolina Agricultural Research Service, Raleigh, NC.

This investigation was supported in part by funds from USDA, ARS cooperative agreement No. 58-7B30-0-209.

We gratefully acknowledge Dr. M.E. Saltveit for the idea that led to the design of the diffusion apparatus and Dr. I.S. Longmuir for helpful discussions that led to an interpretation of diffusion rates

through fresh and brined cucumbers.

Mention of a trademark or proprietary product does not constitute a guarantee or warranty of the product by the U.S. Dept. of Agriculture or North Carolina Agricultural Research Service, nor does it imply approval to the exclusion of other products that may